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(54) **Improved double metal cyanide complex catalysts.**

(57) Improved double metal cyanide catalysts are disclosed. The substantially amorphous catalysts of the invention are more active for polymerizing epoxides than conventional DMC catalysts, which have a substantial crystalline component. Polyol products made with the catalysts are unusually clear, have exceptionally low unsaturations, and contain no detectable amount of low molecular weight polyol impurities. A method of making the improved DMC catalysts, which involves intimately combining the reactants, is also disclosed.

FIELD OF THE INVENTION:

The invention relates to double metal cyanide (DMC) complex catalyst compositions. The catalysts are highly active in epoxide polymerizations. The invention includes an improved method for preparing the compositions. Polyether polyol products made using the catalyst compositions have exceptionally low unsaturations.

BACKGROUND OF THE INVENTION:

Double metal cyanide complex compounds are well known catalysts for epoxide polymerization. The catalysts are highly active, and give polyether polyols that have low unsaturation compared with similar polyols made using basic (KOH) catalysis. Conventional DMC catalysts are prepared by reacting aqueous solutions of metal salts and metal cyanide salts to form a precipitate of the DMC compound. The catalysts can be used to make a variety of polymer products, including polyether, polyester, and polyetherester polyols. Many of the polyols are useful in various polyurethane coatings, elastomers, sealants, foams, and adhesives.

Conventional DMC catalysts are usually prepared in the presence of a low molecular weight complexing agent, typically an ether such as glyme (dimethoxy-ethane) or diglyme. The ether complexes with the DMC compound, and favorably impacts the activity of the catalyst for epoxide polymerization. In one conventional preparation, aqueous solutions of zinc chloride (excess) and potassium hexacyanocobaltate are combined by simple mixing. The resulting precipitate of zinc hexacyanocobaltate is then mixed with aqueous glyme. An active catalyst is obtained that has the formula:



Other known complexing agents include alcohols, ketones, esters, amides, ureas, and the like. (See, for example, U.S. Patent Nos. 3,427,256, 3,427,334, 3,278,459, and Japanese Pat. Appl. Kokai Nos. 4-145123, 3-281529 and 3-149222). Generally, the catalyst made with glyme has been the catalyst of choice. The catalysts have relatively high surface areas, typically within the range of about 50-200 m²/g.

Double metal cyanide compounds prepared in the absence of a complexing agent are highly crystalline (as shown by X-ray diffraction analysis), and are inactive for epoxide polymerization. When the complexing agents described above are used, the resulting catalysts actively polymerize epoxides. Our X-ray diffraction analyses of active DMC complexes prepared according to methods known in the art suggest that conventional DMC catalysts are actually mixtures of a highly crystalline DMC compound and a more amorphous component. Typically, conventional DMC catalysts—which are generally prepared by simple mixing—contain at least about 35 wt. % of highly crystalline DMC compound. DMC compounds useful as epoxide polymerization catalysts and containing less than about 30 wt. % of highly crystalline DMC compound are not known.

Double metal cyanide catalysts generally have good activity for epoxide polymerizations, often much greater than conventional basic catalysts. However, because the DMC catalysts are rather expensive, catalysts with improved activity are desirable because reduced catalyst levels could be used.

Double metal cyanide catalysts normally require an "induction" period. In contrast to basic catalysts, DMC catalysts ordinarily will not begin polymerizing epoxides immediately following exposure of epoxide and starter polyol to the catalyst. Instead, the catalyst needs to be activated with a small proportion of epoxide before it becomes safe to begin continuously adding the remaining epoxide. Induction periods of an hour or more are typical yet costly in terms of increased cycle times in a polyol production facility. Reduction or elimination of the induction period is desirable.

An advantage of DMC catalysts is that they permit the synthesis of high molecular weight polyether polyols having relatively low unsaturation. The adverse impact of polyol unsaturation on polyurethane properties is well documented. (See, for example, C.P. Smith et al., *J. Elast. Plast.*, 24 (1992) 306, and R.L. Mascioli, *SPI Proceedings, 32nd Annual Polyurethane Tech./Market. Conf.* (1989) 139.) When a DMC catalyst is used, polyols having unsaturations as low as about 0.015 meq/g can be made. Polyether polyols with even lower unsaturations can be made if a solvent such as tetrahydrofuran is used to make the polyol. However, for commercial polyol production, the use of a solvent is not particularly desirable. Thus, other ways to further reduce polyol unsaturation are needed.

When conventional DMC catalysts are used to polymerize epoxides, the polyether polyol products contain relatively low levels (about 5-10 wt. %) of low molecular weight polyol impurities. A way to eliminate these polyol impurities is desirable because improved polyurethanes could result from the use of more monodisperse polyols.

Double metal cyanide complex catalyst residues are often difficult to remove from polyether polyols, and a wide variety of methods have been developed to cope with the problem. Removal of DMC catalyst residues from the polyols promotes long-term storage stability and consistent polyol performance in urethane formula-

tion. Most methods involve some kind of chemical treatment of the polyol following polymerization. There has been little progress made in developing catalyst preparation methods that ultimately facilitate catalyst removal from the polyol products.

5 SUMMARY OF THE INVENTION:

The invention is an improved catalyst for polymerizing epoxides. We have surprisingly found that substantially amorphous DMC complexes are much more active than conventional DMC complexes for epoxide polymerization. In addition, the amorphous complexes are more quickly activated (show reduced induction periods) compared with conventional DMC catalysts.

10 The catalysts of the invention comprise at least about 70 wt. % of a substantially amorphous DMC complex; more preferred compositions comprise from about 90-99 wt. % of the substantially amorphous DMC complex.

The invention also includes compositions which comprise the substantially amorphous DMC complexes described above, and up to about 30 wt. % of a highly crystalline DMC compound; more preferred compositions 15 contain less than about 1 wt. % of the highly crystalline DMC compound.

The invention includes a method for preparing the improved catalysts. Although conventional methods for making DMC complex catalysts have been known for about 30 years, no one has previously appreciated that the method of combining the reactants is extremely important. We have now discovered, quite surprisingly, that highly active, substantially amorphous DMC complexes are produced only when the reactants are intimately combined during catalyst preparation. Aqueous solutions of a water-soluble metal salt and a water-soluble metal cyanide salt are intimately combined in the presence of a complexing agent to produce an aqueous mixture containing the DMC complex catalyst. The catalyst, which is then isolated and dried, comprises at least 20 about 70 wt. % of a substantially amorphous DMC complex.

The invention also includes a method for preparing an epoxide polymer. The method comprises polymerizing an epoxide in the presence of a catalyst which comprises at least about 70 wt. % of a substantially amorphous DMC complex.

The invention also includes polyether polyol compositions that are uniquely available from using the catalysts of the invention. The polyols have exceptionally low unsaturations and contain unusually low-levels of low molecular weight polyol impurities.

30 Finally, the invention includes a method for improving the filterability of a DMC complex catalyst from a polyether polyol product following epoxide polymerization. The method comprises using, as a polymerization catalyst, a substantially amorphous DMC complex catalyst of the invention.

BRIEF DESCRIPTION OF THE DRAWING:

35 Figure 1 shows a plot of propylene oxide consumption versus time during a polymerization reaction with one of the catalyst compositions of the invention at 250 ppm catalyst. The induction time for the run is measured as discussed in Example 6 from the intersection of the extended baseline and slope measurements.

40 DETAILED DESCRIPTION OF THE INVENTION:

The catalysts of the invention, unlike conventional DMC compounds known in the art as useful for epoxide polymerization, comprise at least about 70 wt. % of a substantially amorphous DMC complex. More preferred catalysts of the invention comprise at least about 90 wt. % of a substantially amorphous DMC complex; most preferred are catalysts comprising at least about 99 wt. % of a substantially amorphous DMC complex.

45 As defined in this application, "substantially amorphous" means substantially noncrystalline, lacking a well-defined crystal structure, or characterized by the substantial absence of sharp lines in the X-ray diffraction pattern of the composition. Powder X-ray diffraction (XRD) patterns of conventional double metal cyanide catalysts show characteristic sharp lines that correspond to the presence of a substantial proportion of a highly crystalline DMC component. Highly crystalline zinc hexacyanocobaltate prepared in the absence of an organic complexing agent, which does not actively polymerize epoxides, shows a characteristic XRD fingerprint of sharp lines at d-spacings of about 5.07, 3.59, 2.54, and 2.28 angstroms.

50 When a DMC catalyst is made in the presence of an organic complexing agent according to conventional methods, the XRD pattern shows lines for the highly crystalline material in addition to broader signals from relatively amorphous material, suggesting that conventional DMC epoxidation catalysts are actually mixtures of highly crystalline DMC compound and a more amorphous component. Typically, conventional DMC catalysts, which are generally prepared by simple mixing, contain at least about 35 wt. % of highly crystalline DMC compound.

The catalysts of the invention are distinguishable from conventional DMC compositions based on their substantial lack of crystalline material. The substantial lack of crystallinity is evidenced by an XRD pattern showing that little or no highly crystalline DMC compound is present. When a zinc hexacyanocobaltate catalyst is prepared according to the method of the invention using tert-butyl alcohol as a complexing agent, for example, the X-ray diffraction pattern shows essentially no lines for crystalline zinc hexacyanocobaltate (5.07, 3.59, 2.54, 2.28 angstroms), but instead has only two major lines, both relatively broad, at d-spacings of about 4.82 and 3.76 angstroms. Spiking experiments demonstrate that DMC catalysts prepared by the method of the invention typically contain less than about 1 wt.% of highly crystalline DMC compound. X-ray results appear in Table 1.

Conventional DMC catalysts typically contain at least about 35 wt.% of highly crystalline DMC compound. No one has previously recognized the desirability of preparing substantially amorphous catalysts, and the potential value of reducing the content of highly crystalline DMC compounds in these catalysts. It appears, based on my results, that the highly crystalline DMC compound acts as either a diluent or as a poison for the more active amorphous form of the catalyst, and its presence is preferably minimized or eliminated.

The invention includes compositions which comprise at least about 70 wt.% of the substantially amorphous DMC complex catalysts of the invention and up to about 30 wt.% of a highly crystalline DMC compound. More preferred compositions of the invention comprise at least about 90 wt.% of the substantially amorphous DMC complex catalyst and up to about 10 wt.% of the highly crystalline DMC compound. Most preferred are compositions that contain at least about 99 wt.% of the substantially amorphous DMC complex catalyst and up to about 1 wt.% of the highly crystalline material.

The catalyst compositions of the invention have relatively low surface areas. Conventional DMC compounds have surface areas within the range of about 50 to about 200 m²/g. In contrast, the surface areas of the catalysts of the invention are preferably less than about 30 m²/g. More preferred compositions have surface areas less than about 20 m²/g.

Double metal cyanide compounds useful in the invention are the reaction products of a water-soluble metal salt and a water-soluble metal cyanide salt. The water-soluble metal salt preferably has the general formula M(X)_n in which M is selected from the group consisting of Zn(II), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(IV), Sr(II), W(IV), W(VI), Cu(II), and Cr(III). More preferably, M is selected from the group consisting of Zn(II), Fe(II), Co(II), and Ni(II). In the formula, X is preferably an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate, and nitrate. The value of n is from 1 to 3 and satisfies the valency state of M. Examples of suitable metal salts include, but are not limited to, zinc chloride, zinc bromide, zinc acetate, zinc acetoxyacetate, zinc benzoate, zinc nitrate, iron(II) sulfate, iron(II) bromide, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) formate, nickel(II) nitrate, and the like, and mixtures thereof.

The water-soluble metal cyanide salts used to make the double metal cyanide compounds useful in the invention preferably have the general formula (Y)_aM'(CN)_b(A)_c in which M' is selected from the group consisting of Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV), and V(V). More preferably, M' is selected from the group consisting of Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III), and Ni(II). The water-soluble metal cyanide salt can contain one or more of these metals. In the formula, Y is an alkali metal ion or alkaline earth metal ion. A is an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate, and nitrate. Both a and b are integers greater than or equal to 1; the sum of the charges of a, b, and c balances the charge of M'. Suitable water-soluble metal cyanide salts include, but are not limited to, potassium hexacyanocobaltate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III), lithium hexacyanoferrate(III), and the like.

Examples of double metal cyanide compounds that can be used in the invention include, for example, zinc hexacyanocobaltate(III), zinc hexacyanoferrate(III), zinc hexacyanoferrate(II), nickel(II) hexacyanoferrate(II), cobalt(II) hexacyanocobaltate(III), and the like. Further examples of suitable double metal cyanide compounds are listed in U.S. Patent No. 5,158,922, the teachings of which are incorporated herein by reference.

The catalyst compositions of the invention are prepared in the presence of a complexing agent. Generally, the complexing agent must be relatively soluble in water. Suitable complexing agents are those commonly known in the art, as taught, for example, in U.S. Patent No. 5,158,922. The complexing agent is added either during preparation or immediately following precipitation of the catalyst. Usually, an excess amount of the complexing agent is used. Preferred complexing agents are water-soluble heteroatom-containing organic compounds that can complex with the double metal cyanide compound. Suitable complexing agents include, but are not limited to, alcohols, aldehydes, ketones, ethers, esters, amides, ureas, nitriles, sulfides, and mixtures thereof. Preferred complexing agents are water-soluble aliphatic alcohols selected from the group consisting of ethanol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, and tert-butyl alcohol.

The conventional method of preparing DMC compounds useful for epoxide polymerization is fully described in many references, including U.S. Patent Nos. 5,158,922, 4,843,054, 4,477,589, 3,427,335, 3,427,334, 3,427,256, 3,278,457, and 3,941,849, and Japanese Pat. Appl. Kokai No. 4-145123. The teachings of these references related to conventional catalyst preparation and suitable DMC compounds are incorporated herein by reference in their entirety.

The invention includes a method of making the substantially amorphous DMC catalyst compositions of the invention. The method comprises two steps. First, aqueous solutions of a water-soluble metal salt and a water-soluble metal cyanide salt are intimately combined and reacted in the presence of a complexing agent to produce an aqueous mixture that contains a precipitated DMC complex catalyst. Second, the catalyst is isolated and dried. The complexing agent can be included with either or both of the aqueous salt solutions, or it can be added to the DMC compound immediately following precipitation of the catalyst. It is preferred to pre-mix the complexing agent with either the water-soluble metal cyanide salt, or with the water-soluble metal salt, or both, before intimately combining the reactants. The resulting catalyst composition is substantially amorphous, as is evidenced by the substantial absence of highly crystalline DMC compound by X-ray diffraction analysis.

We have surprisingly discovered that achieving an intimate combination of the reactants is essential to preparing catalysts having low crystallinity. In conventional methods, the water-soluble metal salt and the water-soluble metal cyanide salt are combined in aqueous media and are simply mixed together, typically with magnetic or mechanical stirring. This method of preparation results in catalysts having a substantial amount of highly crystalline DMC component, typically greater than about 35 wt.%. We have found that combining the reactants in a manner effective to achieve an intimate combination of the reactants results in substantially amorphous catalysts that are exceptionally useful for epoxide polymerization. Suitable methods of achieving this intimate combination of reactants include homogenization, impingement mixing, high-shear stirring, and the like. When the reactants are homogenized, for example, the level of crystalline material in the catalyst composition is minimized or eliminated, and is much lower than the amount of crystalline material present in a catalyst made by simple mixing.

The invention includes a process for making an epoxide polymer. This process comprises polymerizing an epoxide in the presence of a double metal cyanide catalyst composition of the invention. Preferred epoxides are ethylene oxide, propylene oxide, butene oxides, styrene oxide, and the like, and mixtures thereof. The process can be used to make random or block copolymers. The epoxide polymer can be, for example, a polyether polyol derived from the polymerization of an epoxide in the presence of a hydroxyl group-containing initiator.

Other monomers that will copolymerize with an epoxide in the presence of a DMC compound can be included in the process of the invention to make other types of epoxide polymers. Any of the copolymers known in the art made using conventional DMC catalysts can be made with the catalysts of the invention. For example, epoxides copolymerize with oxetanes (as taught in U.S. Patent Nos. 3,278,457 and 3,404,109) to give polyethers, or with anhydrides (as taught in U.S. Patent Nos. 5,145,883 and 3,538,043) to give polyester or polyetherester polyols. The preparation of polyether, polyester, and polyetherester polyols using double metal cyanide catalysts is fully described, for example, in U.S. Patent Nos. 5,223,583, 5,145,883, 4,472,560, 3,941,849, 3,900,518, 3,538,043, 3,404,109, 3,278,458, 3,278,457, and in J.L. Schuchardt and S.D. Harper, SPI Proceedings, 32nd Annual Polyurethane Tech./Market Conf. (1989) 360. The teachings of these references related to polyol synthesis using DMC catalysts are incorporated herein by reference in their entirety.

The amorphous DMC catalysts of the invention are highly active compared to conventional DMC catalysts (see Table 2). For example, a zinc hexacyanocobaltate catalyst made using tert-butyl alcohol as a complexing agent and made by homogenization (and containing less than 1 wt.% of crystalline DMC compound by X-ray analysis) is about 65% more active at 100 ppm, and 200% more active at 130-250 ppm, than the same catalyst made by simple mixing (and containing about 35 wt.% crystalline DMC compound). A consequence of higher polymerization rates is that polyol producers can use less of the relatively expensive DMC catalyst and save money. More active catalysts also permit the producer to reduce batch times and increase productivity.

The amorphous catalyst compositions of the invention show a reduced induction period compared with conventional catalysts in a polyether polyol synthesis (see Table 3). Conventional DMC catalysts are not immediately active toward epoxide polymerization. Typically, a starter polyol, the catalyst, and a small amount of epoxide are combined and heated to the desired reaction temperature, and no epoxide polymerizes immediately. The polyol manufacturer must wait (often for several hours) until the catalyst becomes active and the charged epoxide begins to react before additional epoxide can safely be continuously added to the polymerization reactor. The substantially amorphous catalysts of the invention are more rapidly activated than conventional catalysts that contain up to 35 wt.% of crystalline DMC compound. This feature of the catalysts is also an economic advantage because delays in adding the epoxide are reduced.

Polyether polyols prepared using the catalysts of the invention have exceptionally low unsaturations, consistently less than about 0.007 meq/g. These unsaturations are at least about 50% lower than polyol unsaturations.

ations available from the DMC catalysts previously known (see Table 4). Preferred polyols of the invention have unsaturations less than about 0.006 meq/g, and more preferably less than about 0.005 meq/g. The reduction in unsaturation compared with polyols previously available from conventional DMC catalysts should offer some advantages for polyurethanes made with the polyols of the invention.

5 Polyether polyols made with the catalysts of the invention preferably have average hydroxyl functionalities from about 2 to 8, more preferably from about 2 to 6, and most preferably from about 2 to 3. The polyols preferably have number average molecular weights within the range of about 500 to about 50,000. A more preferred range is from about 1,000 to about 12,000; most preferred is the range from about 2,000 to about 8,000.

10 Polyols prepared with the catalysts of the invention also have substantially lower levels of low molecular weight polyol impurities compared with polyols prepared with conventional catalysts. Gel permeation chromatography (GPC) analysis of these polyols shows no detectable low molecular weight polyol impurities. In contrast, conventional DMC catalysts made in the usual way with glyme as a complexing agent show a marked GPC peak corresponding to about 5-10 wt.% of a low molecular weight polyol impurity.

15 Interestingly, polyols made with the catalysts of the invention are usually clearer than polyols made with conventional glyme catalysts; the former typically remain clear even after weeks of storage at room temperature, while the latter tend to quickly develop a haze during storage.

Another advantage of the substantially amorphous catalysts of the invention is that they are more easily removed from polyether polyols following polyol synthesis compared with conventional DMC compounds. The problem of how to remove DMC compounds from polyether polyols has been the subject of many investigations (see, for example, U.S. Patent Nos. 5,144,093, 5,099,075, 5,010,047, 4,987,271, 4,877,906, 4,721,818, and 4,355,188). Most of these methods irreversibly deactivate the catalyst.

20 The catalysts of the invention can be isolated by simply filtering the polyol. Another way to isolate the catalyst is to first dilute the polyol with a solvent such as heptane to reduce viscosity, then filter the mixture to recover the catalyst, and then strip the polyol/heptane mixture to obtain the purified polyol. The methods described in U.S. Patent No. 5,010,047 can also be used to recover the catalysts of the invention from polyols. An advantage of the catalysts of the invention is that they can be removed cleanly from polyols even with a hot filtration in the absence of any solvent. In contrast, when a polyol made with a conventional glyme catalyst is hot-filtered, substantial amounts of the DMC compound remain in the polyol. If desired, the isolated catalyst composition of the invention can be recovered and reused to catalyze another epoxide polymerization reaction because these simple filtration methods do not generally deactivate the catalysts.

30 The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

Preparation of Zinc Hexacyanocobaltate Catalysts by Homogenization

Example 1. Tert-butyl Alcohol as the Complexing Agent (Catalyst D)

35 Potassium hexacyanocobaltate (8.0 g) is added to deionized water (150 mL) in a beaker, and the mixture is blended with a homogenizer until the solids dissolve. In a second beaker, zinc chloride (20 g) is dissolved in deionized water (30 mL). The aqueous zinc chloride solution is combined with the solution of the cobalt salt using a homogenizer to intimately mix the solutions. Immediately after combining the solutions, a mixture of tert-butyl alcohol (100 mL) and deionized water (100 mL) is added slowly to the suspension of zinc hexacyanocobaltate, and the mixture is homogenized for 10 min. The solids are isolated by centrifugation, and are then homogenized for 10 min. with 250 mL of a 70/30 (v:v) mixture of tert-butyl alcohol and deionized water. 45 The solids are again isolated by centrifugation, and are finally homogenized for 10 min with 250 mL of tert-butyl alcohol. The catalyst is isolated by centrifugation, and is dried in a vacuum oven at 50°C and 30 in. (Hg) to constant weight. This catalyst is identified as Catalyst D.

Preparation of Zinc Hexacyanocobaltate Catalysts by Homogenization

Example 2. Isopropyl Alcohol as the Complexing Agent (Catalyst E)

50 The procedure of Example 1 is modified as follows. Isopropyl alcohol is substituted for tert-butyl alcohol. Following combination of the zinc chloride and potassium hexacyanocobaltate solutions and homogenization in the presence of isopropyl alcohol, the catalyst slurry is filtered through a 0.45 micron filter at 20 psi. The washing steps of Example 1 are also repeated, but filtration rather than centrifugation is used to isolate the catalyst. The washed catalyst is dried to constant weight as described above. The catalyst is identified as Catalyst E.

Preparation of Zinc Hexacyanocobaltate Catalysts by Simple MixingComparative Example 3. Tert-butyl Alcohol as the Complexing Agent (Catalyst B)

5 The procedure of Japanese Pat. Appl. Kokai No. 4-145123 is generally followed. Potassium hexacyano-
cobaltate (4.0 g) is added to deionized water (75 mL) in a beaker, and the mixture is stirred until the solids
dissolve. In a second beaker, zinc chloride (10 g) is dissolved in deionized water (15 mL). The aqueous zinc
chloride solution is combined with the solution of the cobalt salt using a magnetic stirring bar to mix the solu-
10 tions. Immediately after combining the solutions, a mixture of tert-butyl alcohol (50 mL) and deionized water
(50 mL) is added slowly to the suspension of zinc hexacyanocobaltate, and the mixture is stirred for 10 min.
The solids are isolated by centrifugation, and are then stirred for 10 min. with 100 mL of a 70/30 (v:v) mixture
of tert-butyl alcohol and deionized water. The solids are again isolated by centrifugation, and are finally stirred
for 10 min with 100 mL of tert-butyl alcohol. The catalyst is isolated by centrifugation, and is dried in a vacuum
oven at 50°C and 30 in. (Hg) to constant weight. This catalyst is identified as Catalyst B.

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Preparation of Zinc Hexacyanocobaltate Catalysts by Simple MixingComparative Example 4. Isopropyl Alcohol as the Complexing Agent (Catalyst C)

20 The procedure of Comparative Example 3 is followed, except that isopropyl alcohol is used in place of tert-
butyl alcohol, and the solids are isolated by filtration using a 0.8 micron filter rather than by centrifugation.
The catalyst is isolated and dried as described above. This catalyst is identified as Catalyst C.

25 Comparative Example 5. Preparation of Crystalline Zinc Hexacyanocobaltate No Complexing Agent (Cata-
lyst A)

Potassium hexacyanocobaltate (4.0 g) is dissolved in deionized water (150 mL) in a beaker. Zinc chloride
(10 g) is dissolved in deionized water (15 mL) in a second beaker. The aqueous solutions are quickly combined
and magnetically stirred for 10 min. The precipitated solids are isolated by centrifugation. The solids are re-
30 slurried in deionized water (100 mL) for 10 min. with stirring, and are again recovered by centrifugation. The
catalyst is dried in a vacuum oven at 50°C and 30 in. (Hg) to constant weight. This catalyst is identified as Cat-
alyst A.

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Example 6. Epoxide Polymerizations: Rate Experiments-- General Procedure

A one-liter stirred reactor is charged with polyoxypropylene triol (700 mol. wt.) starter (70 g) and zinc hex-
acyanocobaltate catalyst (0.057 to 0.143 g, 100-250 ppm level in finished polyol, see Table 2). The mixture is
stirred and heated to 105°C, and is stripped under vacuum to remove traces of water from the triol starter.
The reactor is pressurized to about 1 psi with nitrogen. Propylene oxide (10-11 g) is added to the reactor in
40 one portion, and the reactor pressure is monitored carefully. Additional propylene oxide is not added until an
accelerated pressure drop occurs in the reactor; the pressure drop is evidence that the catalyst has become
activated. When catalyst activation is verified, the remaining propylene oxide (490 g) is added gradually over
about 1-3 h at a constant pressure of 20-24 psi. After propylene oxide addition is complete, the mixture is held
at 105°C until a constant pressure is observed. Residual unreacted monomer is then stripped under vacuum
45 from the polyol product, and the polyol is cooled and recovered.

To determine reaction rate, a plot of PO consumption (g) vs. reaction time (min) is prepared (see Fig. 1).
The slope of the curve at its steepest point is measured to find the reaction rate in grams of PO converted per
minute. The intersection of this line and a horizontal line extended from the baseline of the curve is taken as
the induction time (in minutes) required for the catalyst to become active. The results of reaction rates and
50 induction times measured for various catalysts at 100-250 ppm catalyst levels appear in Tables 2 and 3.

Example 7. Polyether Polyol Synthesis: Effect of Catalyst on Polyol Unsaturation, Catalyst Removal, and
Polyol Quality

55 A two-gallon stirred reactor is charged with polyoxypropylene triol (700 mol. wt.) starter (685 g) and zinc
hexacyanocobaltate catalyst (1.63 g). The mixture is stirred and heated to 105°C, and is stripped under vacuum
to remove traces of water from the triol starter. Propylene oxide (102 g) is fed to the reactor, initially under a
vacuum of 30 in. (Hg), and the reactor pressure is monitored carefully. Additional propylene oxide is not added

until an accelerated pressure drop occurs in the reactor; the pressure drop is evidence that the catalyst has become activated. When catalyst activation is verified, the remaining propylene oxide (5713 g) is added gradually over about 2 h while maintaining a reactor pressure less than 40 psi. After propylene oxide addition is complete, the mixture is held at 105°C until a constant pressure is observed. Residual unreacted monomer is then stripped under vacuum from the polyol product. The hot polyol product is filtered at 100°C through a filter cartridge (0.45 to 1.2 microns) attached to the bottom of the reactor to remove the catalyst. Residual Zn and Co are quantified by X-ray analysis.

Polyether diols (from polypropylene glycol starter, 450 mol. wt.) and triols are prepared as described above using zinc hexacyanocobaltate catalysts made by conventional methods (stirring) and by the method of the invention (homogenization). The impact of the catalysts of the invention on epoxide polymerization rate (Table 2), induction period (Table 3), polyol unsaturation (Table 4), catalyst removal (Table 5), and polyol quality (Table 6) are shown in the tables.

The preceding examples are meant only as illustrations. The scope of the invention is defined by the claims.

Table 1. DMC Catalyst Characterization

ID	Catalyst	X-Ray Diffraction Pattern (d-spacings, angstroms) ¹						Surface area (m ² /g)
		5.07	4.82	3.76	3.59	2.54	2.28	
A	Cryst. Zn-Co ²	X	absent	absent	X	X	X	454
B	TBA stirred ²	X	X	X	X	X	X	82
C	IPA stirred ²	X	absent	X	X	X	X	n.m.
D	TBA homog.	absent	X	X	absent	absent	absent	14
E	IPA homog.	absent	X	X	absent	absent	absent	n.m.

X = X-ray diffraction line present; n.m. = not measured.

Samples were analyzed by X-ray diffraction using monochromatized CuK α_1 radiation ($\lambda = 1.54059 \text{ \AA}$). A Seimens D500 Kristalloflex diffractometer powered at 40 kV and 30 mA was operated in a step scan mode of $0.02^\circ 2\theta$ with a counting time of 2 seconds/step. Divergence slits of 1° in conjunction with monochromator and detector apertures of 0.05° and 0.15° respectively. Each sample was run from 5° to $70^\circ 2\theta$.

¹ Water of hydration can cause minor variations in measured d-spacings.

² Comparative example.

³ Catalyst of the invention.

Table 2. Effect of Catalyst on Epoxide Polymerization Rate (105°C)

I D	Catalyst	Cat. amt. (ppm)	Rate of polymerization (g/min)
F	glyme ^{1,2}	250	3.50
		130	1.78
		100	1.46
B	TBA stirred ²	250	3.64
		130	2.50
		100	2.29
D	TBA homog. ³	250	10.5
		130	7.40
		100	3.84
C	IPA stirred ²	250	0.3
E	IPA homog. ³	250	1.70

¹ Catalyst F is prepared as described in U.S. Patent No. 5,158,922.

² Comparative example.

³ Catalyst of the invention.

Table 3. Effect of Catalyst on Induction Period (105°C)

I D	Catalyst	Catalyst concentratio n (ppm)	Induction Time (min)
F	glyme ^{1,2}	100	230
		250	180
B	TBA stirred ²	100	220
		130	180
		250	90
D	TBA homog. ³	100	140
		130	130
		250	85

¹ Catalyst F is prepared as described in U.S. Patent No. 5,158,922.

² Comparative example.

³ Catalyst of the invention.

Table 4. Effect of Catalyst on Polyol Unsaturation

I D	Catalyst	Polyol OH # (mg KOH/g) and functionalit y	Solvent	Polyol unsaturation (meq/g)
F	glyme ^{1,2}	54	none	0.016
		(Triol)	none	0.017
		27	none	0.019
		(Triol)		
		15		
		(Triol)		
B	TBA stirred ²	35	none	0.011
		(Triol)	none	0.010
		27	none	0.011
		(Triol)		
		14		
		(Triol)		
D	TBA homog. ³	27	none	0.005
		(Triol)	none	
		56	none	0.004
		(Diol)	none	0.005
		27	THF	0.004
		(Diol)	heptane	0.003
		14		0.006
		(Diol)		
		31		
		(Triol)		
		12		
		(Triol)		

¹ Catalyst F is prepared as described in U.S. Patent No. 5,158,922.

² Comparative example.

³ Catalyst of the invention.

Table 5. Effect of Catalyst on Catalyst Removal

I D	Catalyst	Polyol OH # (mg KOH/g) and functionalit y	Filtrat ion Temp. (°C)	Solven t	Residual catalyst (ppm)	
					Zn Co	
F	glyme ^{1,2}	27 (Triol)	100	none	28	12
B	TBA stirred ²	25 (Triol)	100	none	6	3
D	TBA homog. ³	25 (Triol)	100	none	5	< 2
		14 (Diol)	100	none	4	< 2
		29 (Diol)	100	none	3	< 2
		14 (Triol)	100	none	4	< 2
		27 (Triol)	25	heptan e	3	< 2
		14 (Diol)	25	heptan e	6	< 2

¹ Catalyst F is prepared as described in U.S. Patent No. 5,158,922.

² Comparative example.

³ Catalyst of the invention.

Table 6. Effect of Catalyst on Polyol Purity and Clarity

I D	Catalyst	Low Mol. Wt. Polyol Impurity (Wt.%, by GPC)	Appearance (25°C, after 3 weeks)
F	glyme	5-10	hazy
D	TBA	none detected	clear

Claims

1. A catalyst comprising at least about 70 wt.% of a substantially amorphous double metal cyanide (DMC) complex.
2. A catalyst according to Claim 1 wherein the catalyst additionally comprises up to about 30 wt.% of a highly crystalline DMC compound.
3. A catalyst according to Claim 1 comprising at least about 90 wt.% of the substantially amorphous DMC complex.
4. A catalyst according to Claim 3 wherein the catalyst additionally comprises up to about 10 wt.% of a highly crystalline DMC compound.
5. A catalyst according to Claim 1 comprising at least about 99 wt.% of the substantially amorphous DMC complex.
6. A catalyst according to Claim 5 wherein the catalyst additionally comprises up to about 1 wt.% of a highly crystalline DMC compound.
7. A catalyst which consists essentially of a substantially amorphous double metal cyanide complex
8. A catalyst according to any one of Claims 1 to 7 wherein the DMC complex is a zinc hexacyanocobaltate.
9. A catalyst according to any one of Claims 1 to 8 prepared in the presence of a water-soluble aliphatic alcohol complexing agent selected from the group consisting of ethanol, isopropyl alcohol, tert-butyl alcohol, sec-butyl alcohol, n-butyl alcohol, and isobutyl alcohol, tert-butyl alcohol being preferred.
10. A catalyst according to Claim 7 which consists essentially of a substantially amorphous zinc hexacyanocobaltate complex, wherein the catalyst is prepared in the presence of a water-soluble aliphatic alcohol complexing agent selected from the group consisting of ethanol, isopropyl alcohol, tert-butyl alcohol, sec-butyl alcohol, n-butyl alcohol, and isobutyl alcohol.
11. A catalyst according to Claim 10 which exhibits an X-ray diffraction pattern of (d-spacing, angstroms): 4.82 (br), 3.76 (br), and exhibits no detectable signals corresponding to highly crystalline zinc hexacyanocobaltate at about (d-spacing, angstroms): 5.07, 3.59, 2.54, 2.28.
12. A catalyst according to any one of Claims 1 to 11 having a surface area of less than about 30 m²/g.
13. A method of making a double metal cyanide (DMC) complex catalyst according to any one of Claims 1 to 12, said method comprising: (a) intimately combining and reacting aqueous solutions of a water-soluble

metal salt and a water-soluble metal cyanide salt in the presence of a complexing agent to produce an aqueous mixture containing a precipitated DMC complex catalyst; and (b) isolating and drying the DMC complex catalyst.

- 5 14. A method according to Claim 13 wherein the aqueous salt solutions are intimately combined by a homogenization process.
15. A method according to Claim 13 or 14 wherein the complexing agent is selected from alcohols, aldehydes, ketones, ethers, esters, amides, ureas, nitriles, sulfides, and mixtures thereof.
- 10 16. A method according to Claim 15 wherein the complexing agent is a water-soluble aliphatic alcohol selected from ethanol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, and mixtures thereof.
- 15 17. A method of preparing an epoxide polymer, said method comprising polymerizing an epoxide in the presence of a catalyst according to any one of Claims 1 to 12.
18. A method according to Claim 17 wherein the epoxide polymer is a polyether polyol.
19. A low-monomer polyether polyol composition prepared using the catalyst of any one of Claims 1 to 12.
- 20 20. A low-monomer polyether polyol composition according to Claim 19 having an unsaturation of less than about 0.006 meq/g.
- 25 21. A method for improving the filterability of a DMC complex catalyst from a polyether polyol product following epoxide polymerization, said method comprising using as a polymerization catalyst the DMC complex of any one of Claims 1 to 12.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 8612

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 090 444 (SHELL) * claims 1,3 * * example 1 * * page 3, line 33 - page 4, line 20 * ---	1,7,8, 13,15-19	B01J27/26 C08G65/10 C08G65/12
X	EP-A-0 555 053 (ARCO) * claim 1 * ---	1	
D,A	US-A-3 427 335 (R. J. HEROLD) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B01J C08G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 6 February 1995	Examiner Thion, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

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